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ACCUMULATION OF HEAVY METALS IN NATIVE PLANTS GROWING NEAR THE PHOSPHATE TREATMENT INDUSTRY, TUNISIA

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Abstract: The enrichment of the phosphates by a humid process can be accompanied with rejects of mud poured in hydrographic network of the region of Gafsa-Metlaoui to Chott El Gharsa. These releases are rich in phosphate and trace elements; the average is around these values: P_2O_5: 10.96 %, Cd: 25.83 ppm, Zn: 260.91 ppm, Cr: 387.7 ppm, Cu: 16 ppm, Ni: 26 ppm and Sr: 717.15 ppm. Soils adjoining these rejects present total concentrations in Cd, Zn and Cr higher to the maximal contents tolerated in soils. A two step sequential extraction showed that heavy metals (Cd, Cr, Cu and Ni) were poorly labile (i.e. not soluble in diluted $CaCl_2$), indicating that their leaching under natural conditions is probably very low. However, extraction with DTPA, $CaCl_2$ and TEA generated significant amounts of metals (mainly Cd and Cu), suggesting that they were potentially mobilizable. However, zinc and strontium are more concentrated in the mobile phase, indicating that the Zn-Sr-solutions are possible in natural conditions.

This study evaluates the potential for phytoremediation of 30 species collected from six localities, growing on a contaminated site of the study area. Plants and the associated soil samples were collected and analyzed for total metals concentrations. While total metals concentrations in soils vary from 1 to 36 ppm Cd, 1.6 to 2463 ppm Zn, 8.5 to 442 ppm Cr, 2.8 to 38.5 ppm Cu, 1 to 31.7 ppm Ni and 144.6 to 1310 ppm Sr, while those in the plants ranged from 0.11 to 82 ppm Cd, 0.5 to 567 ppm Zn, 0.04 to 174.7 ppm Cr, 0.95 to 51.73 ppm Cu, 0.17 to 6.9 ppm Ni and 6 ppm to 2858 ppm Sr. None of the plants were suitable for phytoextraction because no hyperaccumulator was identified. However, plants with a high bioconcentration factor (BCF, metal concentration ratio of plant roots to soil) and low translocation factor (TF, metal concentration ratio of plant leaves to roots) have the potential for phytostabilization. The plants most effective in the accumulation of metals in leaves are *Malva aegyptiaca* (TF=30.7) for Cd, *Frankenia thymifolia* (TF=8.55) for Zn, *Peganum harmala* (TF=29.14) for Cu and *Citrulus sp* (TF=10.42) for Sr.

Anthemis stiparum was most suitable for phytostabilization of contaminated sites with Cd (BCF=23.51). Our study showed that native plant species growing on contaminated sites may have the potential for phytoremediation.

Key words: Phosphate mud, Heavy metals, Soils, Plants, Phytoremediation, Gafsa-Metlaoui area, Tunisia.

1. INTRODUCTION

In Tunisia natural phosphate is extracted and mineral fertilizers are produced. Gafsa Phosphate Company (CPG) has been active in mining for more than a century. The activity of ore beneficiation and production of various mineral fertilizers is more than half a century old. CPG operates seven open cast quarries and one underground mine. Annual production of merchant phosphate in 2007 reached 8 million tons, placing this country the fifth in the world for phosphate production. After having been exporting all its phosphate rock production during the first fifty years of its activity, Tunisia entered into phosphoric acid and mineral fertilizers production and developed this new activity so that it is now processing more than 80% of its phosphate production.

This industry produces releases under the form of:

i) mud discharged into the hydrographical network, and ii) phosphogypsum stored in the form of "Tabia".

These releases are trace elements-rich such as

in Cd, Zn, Cr and Sr, can contaminate the environment receptors like air, water, soils and plants. The overall objectives of this research are:
i) to determine the concentrations of trace elements (Cd, Zn, Cr, Cu, Ni and Sr) in releases, in soil and in plant biomass growing on the contaminated site;
ii) to compare metal concentrations in the leaves, stems and in roots;
iii) and to assess the feasibility to use these plants for phytoremediation purpose. Information obtained from this study should provide insight for using native plants to remediate metal- contaminated sites.
About a hundred analyze major and trace elements of four samples of mud from the washing units of phosphate and about fifty plants with the soil around the roots were performed. For each plant, leaves, stems and roots were analyzed when they were sampled. To assess the availability of heavy metals in soils around roots, 23 soil samples were performed according to the protocol of Maiz et al. (2000), Damian et al. (2008a,b) and Gazdag et al. (2008).

2. MATERIAL AND METHOD

2.1. Site description

Centres' ore mines are scattered throughout the Gafsa-Métlaoui Basin (GMB) in Tunisia. For treatment of phosphate ore, ten washing units are operational throughout the region (Fig. 1): four laundries in Métlaoui sector, one Laundry in Moulares sector, one Laundry in Kef Eddour sector, one Laundry in Redeyef sector and three Laundries in the Eastern sector (M'Dhilla and Sehib).

Tunisian Chemical Group (TCG) is located in the M'Dhilla sector, where phosphogypsum releases are stored near the site.

Mud samples were taken from Kef Eddour, Métlaoui, Sehib and M'Dhilla laundries. Plants and soils were collected in December 2006 at the riversides (Fig. 1) that drain wash discharges.

In the M'Dhilla area sampling was made near the processing of phosphoric acid factory. In addition phosphogypsum was taken from TCG Tabia. Four reference samples providing from non polluted area will be used to make comparisons.

2.2. Sample preparation and chemical analysis

Mineralogical proportions of mud samples and soils were determined by X-ray diffraction (XRD with a Pan-Analytical brand X' PERT PRO type) carried out at the Laboratory of the Mineral Resources and Environment of the Faculty of Sciences of Tunis.

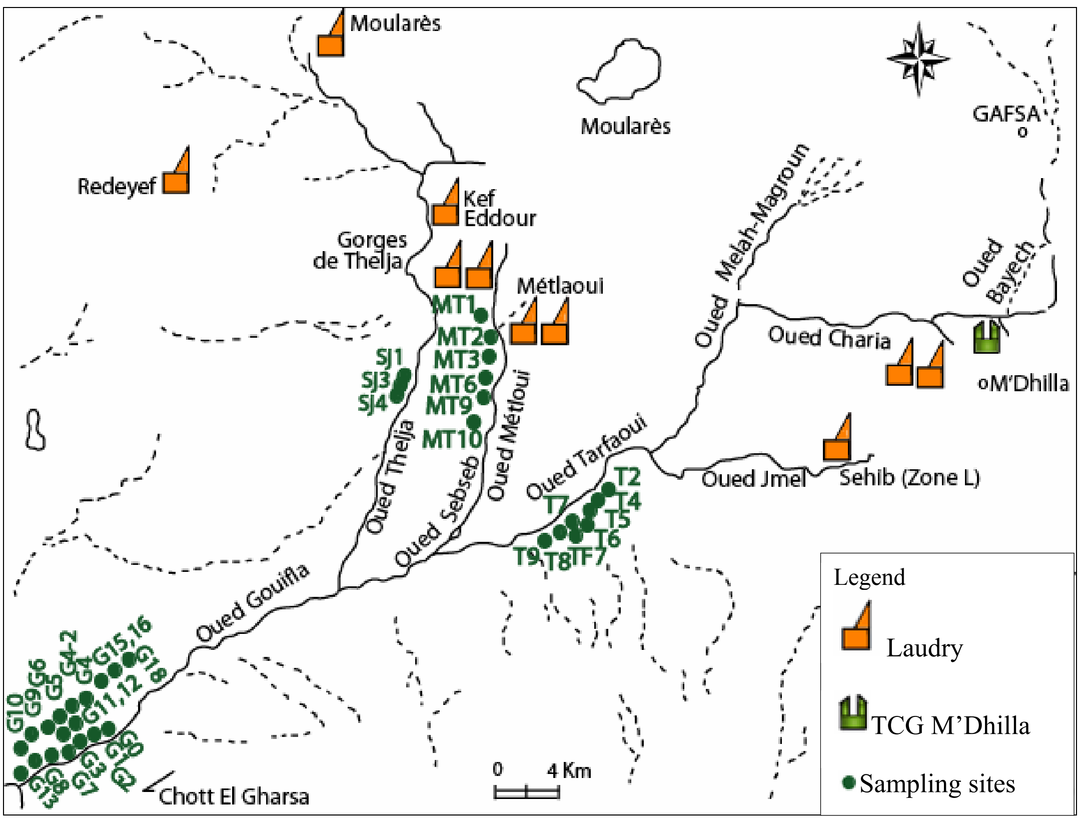

Figure 1: Location of the plants and laundries of Gafsa Phosphates Company (CPG) and the sampling sites in the Gafsa-Métlaoui Basin.

Argillaceous minerals determination was based on oriented clay slides, using three preparations (untreated, glycolated and heated one hour at 550 °C).

Mud and soil samples were analyzed by XRF (X-Ray Fluorescence) for major elements (P, Ca, Si, Al, Fe, Mg, Na, K, and Ti) and ICP-AES (Inductive Coupled Plasma Atomic Emission Spectrometry Activa–Horiba Jobin Yvon Spectrometer) for trace elements (Cd, Zn, Cr, Cu, Ni and Sr) in the Department GENERIC of Ecole Nationale Supérieure des Mines de Saint Etienne. The Soil pH was measured using a 1:2 soil to water ratio. The organic matter was determined by Dorhmann DC 190 at the CRPG-Nancy.

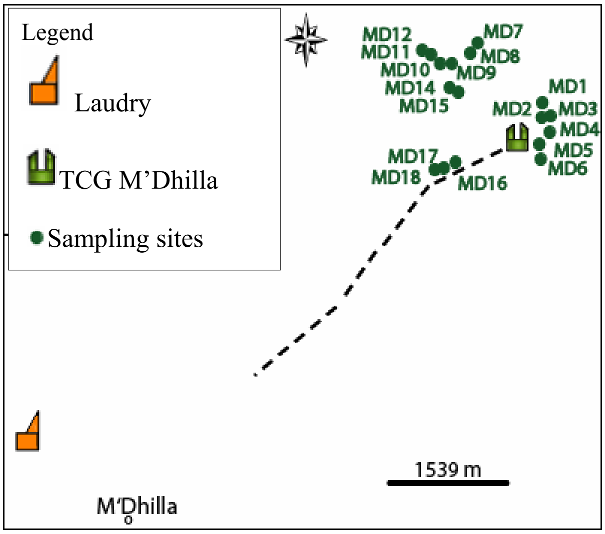

Figure 1. Location of sampling sites rounding M'Dhilla laundry and Gafsa Phosphates Company (CPG) plant.

The evaluation of heavy metals availability was performed using a two steps sequential extraction procedure, as proposed by Maiz et al. (2000). This procedure involved mixing 4 g soil with 20 ml 0.01M $CaCl_2$, under agitation for 24 h at room temperature. This first suspension was centrifuged at 3000 t/min during 15 min, and the supernatant was collected for the analysis of the mobile fraction. The residue was then rinsed two times with ultra pure water and resuspended in 20 ml of 0.005M DTPA, 0.01M $CaCl_2$ and 0.1M TEA, pH 7.3, under continuous agitation for 24 h. After centrifugation at 3000 t/min for 15 minutes, the supernatant was removed and analyzed for the mobilisable fraction. The heavy metals of various extracts were measured by ICP-AES.

Metal accumulation in plant tissues was evaluated from the most abundant species. Plant samples were thoroughly washed in tap water and rinsed three times with distilled water. Samples were then separated into leaves, stems and roots, dried at 40 °C to constant weight and grounded and sieved at 2 mm. Digestion of plant samples was performed using hot nitric concentrated acid, according to Zarcinas et al. (1987), Petrescu et Bilal (2006, 2007), Secu et al. (2008) et Lăcătusu et al. (2009). The plant extracts were analysed by ICP-AES.

3. RESULTS

3.1. Sludge of industry of phosphate

The phosphate laundry factories of Gafsa-Métlaoui Basin reject the muddy fine fraction < 70 µm in the hydrographic network. The mud analyses by XRD show the presence of apatite, calcite, dolomite, quartz, cristobalite and clinoptilolite minerals (Fig. 2A). The clay fraction is represented by the dominant presence of smectite and in lesser amounts by the palygorskite.

The mud chemical composition presents high P_2O_5 contents, 9.5% in the M'Dhilla laundry and 12.4% in the Métlaoui laundry (Table 1). CaO contents vary between 19.4 and 25.6%. SiO_2 contents are also high, with a maximum of 31% in the M'Dhilla mud. Al_2O_3 represented mainly clays contents vary between 5.7% and 7.34%. The percentages of Fe_2O_3 are about 2%, those of MgO showed the highest value (4.3%) in the M'Dhilla mud. Na_2O contents are about 1%. TiO_2 and K_2O show low values (< 1%). These muds are enriched in trace elements and contain an average of Cd: 26 ppm, Zn: 261 ppm, Cr: 388 ppm, Cu: 16 ppm, Ni: 26 ppm and Sr: 718 ppm.

Table 1. Mud chemical composition of laundries; A: Kef Eddour, B: Métlaoui, C: Sehib and D: M'Dhilla and PG: Phosphogypsum composition of Gafsa Phosphates Company plant, LOI*: Loss On Ignition**.**

Elements w%	A	B	C	D	PG
SiO_2	28.63	27.83	26.36	30.91	12.23
TiO_2	0.24	0.22	0.25	0.27	0.02
Al_2O_3	6.23	5.70	5.82	7.34	0.21
Fe_2O_3	2.24	2.08	2.44	2.73	0.20
MgO	2.31	2.22	3.92	4.37	0.22
CaO	25.03	25.65	24.50	19.41	35.42
Na_2O	1.07	0.97	1.15	1.00	0.19
K_2O	0.98	0.92	0.51	0.54	0.07
P_2O_5	11.07	12.43	10.78	9.58	12.02
LOI*	19.86	18.92	21.42	21.20	15.98
Trace-elements ppm					
Cd	26	52	12	14	15
Zn	206	422	200	216	203
Cr	307	498	209	537	33
Cu	13	18	12	21	6
Ni	21	32	16,59	34	2
Sr	680	950	647	594	1325

Phosphogypsum is mainly represented by gypsum and it contains high P_2O_5 (12 wt%) and some trace elements as Cd (15 ppm), Zn (203 ppm), Cr (33 ppm) and Sr (1325 ppm).

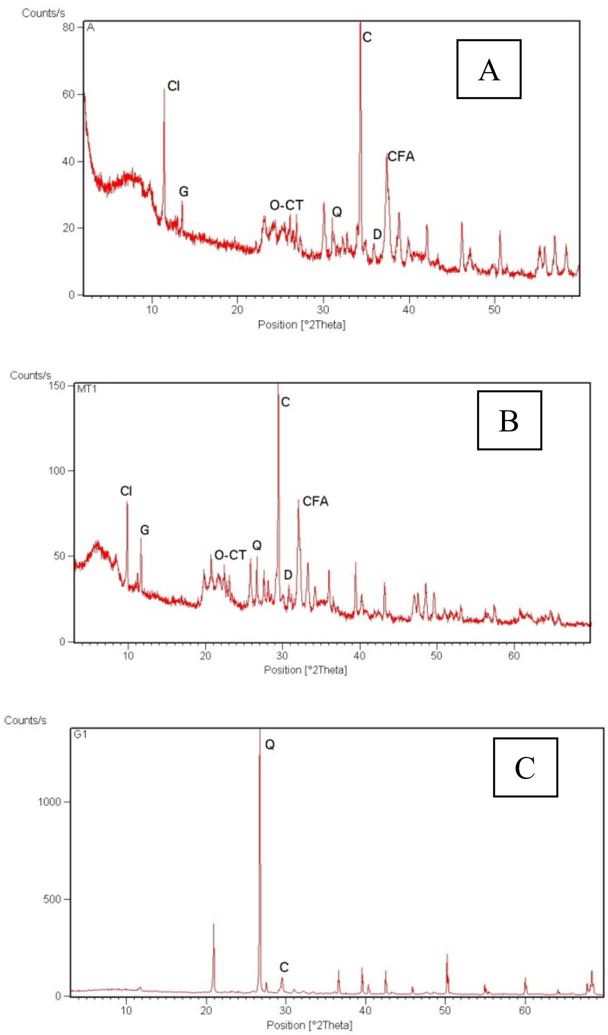

Figure 2. XRays Diffractometric diagrams of powder A: mud of Kef Eddour , B: MT1 soil sample of Métlaoui area and C: G1 soil sample of Chott El Gharsa area. CFA: carbonate fluorapatite, D: dolomite, C: calcite, Q: quartz, O-CT: Opal-CT, G: gypsum and Cl: clinoptilolite.

3.2. Mineralogy and geochemistry of soil

The mineralogical composition of soil samples, collected around the roots, indicates the presence of quartz, calcite, carbonate fluorapatite, dolomite, opal-CT, gypsum and clinoptilolite (Fig. 2B). The majority of soils collected at M'Dhilla Chott El Gharsa and Selja stations, are very enriched in quartz, with the presence of carbonates (calcite and / or dolomite); there is sometimes traces of gypsum and rare phosphate in some samples (Fig. 2C). Soils sampled at the Métlaoui, Tarfaoui and Sehib stations, are silica-rich minerals as quartz, carbonates; there is also a main amount of carbonate-fluorapatite and the presence of clinoptilolite and opal-CT discharges from washing. The reference samples, taken away from the non polluted sites, are sandy, carbonate-rich and mainly gypsum.

The soils are characterized by low levels of organic matter; the maximum (2%) is recorded in the Métlaoui area (MT1 and MT2 samples). The soil pH is slightly alkaline in the various sampling sites except MD4, MD5 and MD6, taken near the treatment of phosphoric acid factory in M’Dhilla which has an acid pH ranging from 4 and 6 (Fig. 3).

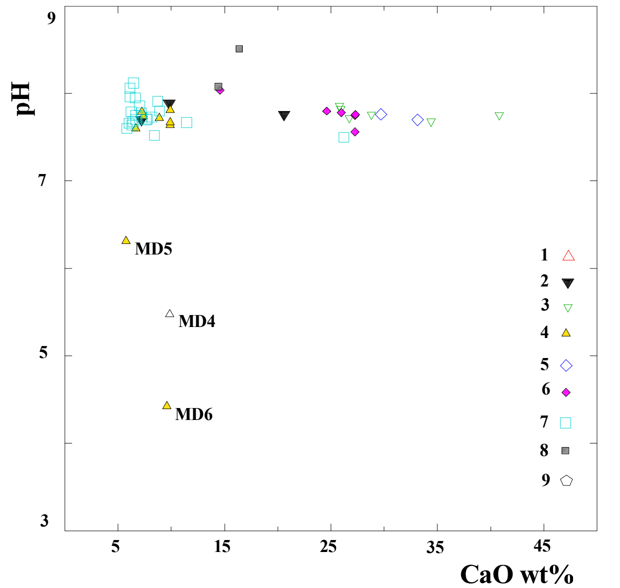

Figure 3. Variation of the pH rate CaO wt% from the soil of Gafsa-Métlaoui Basin. 1: mud; 2: Selja; 3: Métlaoui; 4: M’Dhilla; 5: Sehib; 6: Tarfaoui; 7: Chott El Gharsa; 8: Soil control and 9: Phosphogypsum.

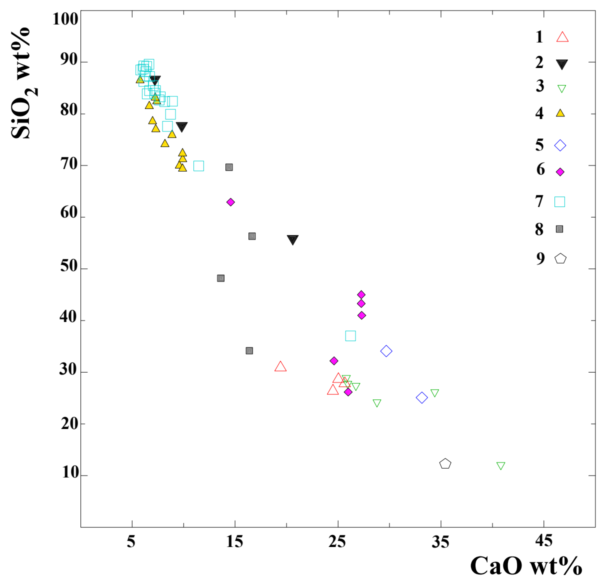

Figure 4. Variation of SiO_2 rate CaO wt% from the soil of Gafsa Métlaoui Basin. 1: mud; 2: Selja; 3: Métlaoui; 4: M’Dhilla; 5: Sehib; 6: Tarfaoui; 7: Chott El Gharsa; 8: Soil control and 9: Phosphogypsum.

The soils of the Gafsa-Métlaoui Basin have quite significant changes; the M'Dhilla and Chott El Gharsa soils are characterized by high levels of SiO_2 above 68% SiO_2 and ratio $(Na_2O+K_2O)/CaO$ (0.05 up to 0.1), however, they have low levels of P_2O_5, Fe_2O_3, MgO, Al_2O_3 and CaO (Figs 4-9) comparatively to Selja, Métlaoui, Sehib and Tarfaoui soils (Figs 10, 11).

- The Selja soils are characterized by low P_2O_5 content of about 1% except Sj1 sample which shows 9%. The CaO contents vary between 7.2 and 9.8 wt% in Sj3 and Sj4 respectively. The highest concentration concerns Sj1 with 20.6 wt% CaO. The SiO_2 contents are the highest (78 and 87 wt%) recorded in the phosphate-poor samples (0.71 wt% and 1.88 wt% P_2O_5). The Al_2O_3 values vary between 1.13 and 2 wt%; those of Fe_2O_3 range between 0.6 and 1 wt%. The concentrations of TiO_2, MgO, Na_2O and K_2O are the lowest, showing values below 1 wt%. The trace metal concentrations vary between 2-22 ppm for Cd, 15-122 ppm for Cr, 2-9 ppm for Ni, 7-9 ppm for Cu and 145-665 ppm for Sr; the maximum value in each element is recorded in SJ1 soil phosphate. Zn shows values ranging from 136 up to 582 ppm.

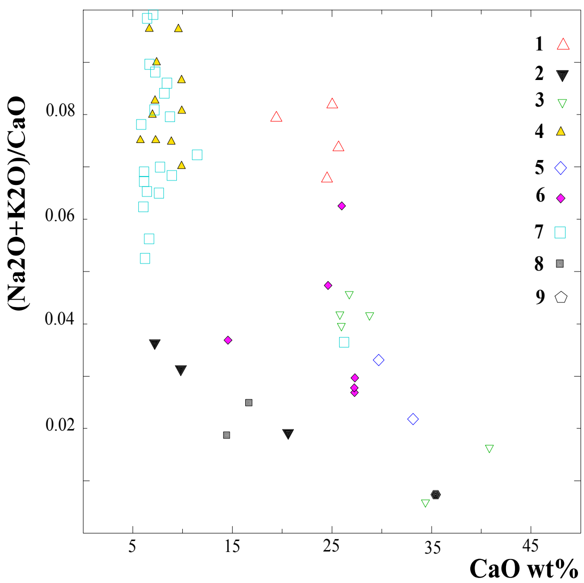

Figure 5. Variation of $(Na_2O+K_2O)/CaO$ versus CaO wt% from the soil of Gafsa-Métlaoui Basin. 1: mud; 2: Selja; 3: Métlaoui; 4: M'Dhilla; 5: Sehib; 6: Tarfaoui; 7: Chott El Gharsa; 8: Soil control and 9: Phosphogypsum.

- The Métlaoui soils are enriched in phosphates; the P_2O_5 contents vary between 10.5% (MT1) and 21.5% (MT2) and those of CaO ranged between 26 and 41% in samples MT1 and MT2, respectively. Silica contents are lower than those recorded in the Selja sector, with a maximum of 29% in MT1. The Al_2O_3 values are interesting, ranging from 1.5% (MT9) and 6% (MT1). The MgO and Fe_2O_3 concentrations are variable ranging from 1% (MT2) and 2% (MT1). TiO_2, Na_2O and K_2O are characterised by low amounts in the soil collected near the wadi Métlaoui. The Cd, Cr, Zn and Sr high values range between 16-36 ppm, 150 - 1299 ppm, 119-443 ppm and 794-1309.9 ppm respectively. Cu and Ni contents are high compared to those analyzed at the Selja respectively, with a maximum of 38.5 and 31 ppm.

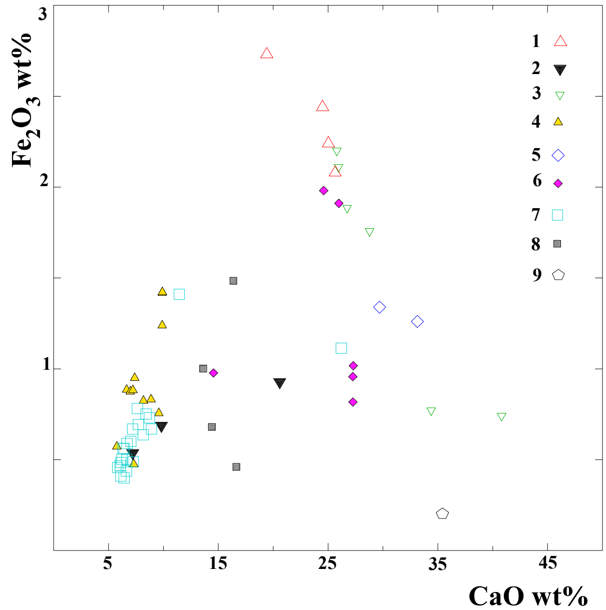

Figure 6. Variation of Fe_2O_3 rate CaO wt% from the soil of Gafsa-Métlaoui Basin. 1: mud; 2: Selja; 3: Métlaoui; 4: M'Dhilla; 5: Sehib; 6: Tarfaoui; 7: Chott El Gharsa; 8: Soil control and 9: Phosphogypsum.

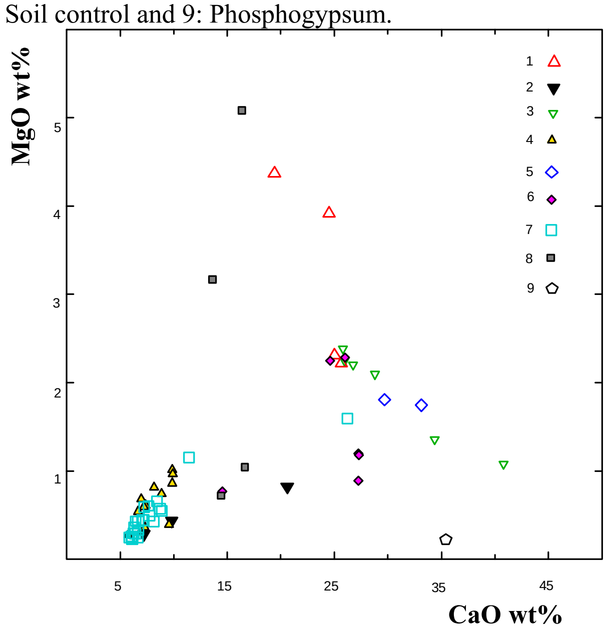

Figure 7. Variation of MgO rate CaO wt% from the soil of Gafsa Métlaoui Basin. 1: mud; 2: Selja; 3: Métlaoui; 4: M'Dhilla; 5: Sehib; 6: Tarfaoui; 7: Chott El Gharsa; 8: Soil control and 9: Phosphogypsum.

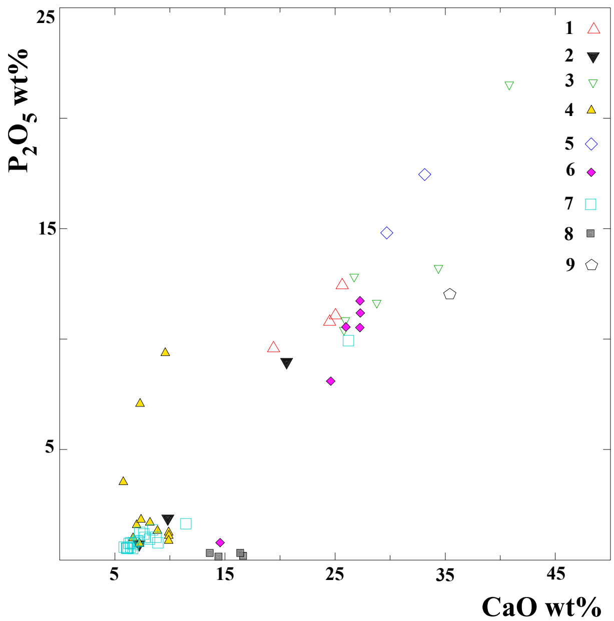

Figure 8. Variation of P_2O_5 rate CaO wt% from the soil of Gafsa-Métlaoui Basin. 1: mud; 2: Selja; 3: Métlaoui; 4: M'Dhilla; 5: Sehib; 6: Tarfaoui; 7: Chott El Gharsa; 8: Soil control and 9: Phosphogypsum.

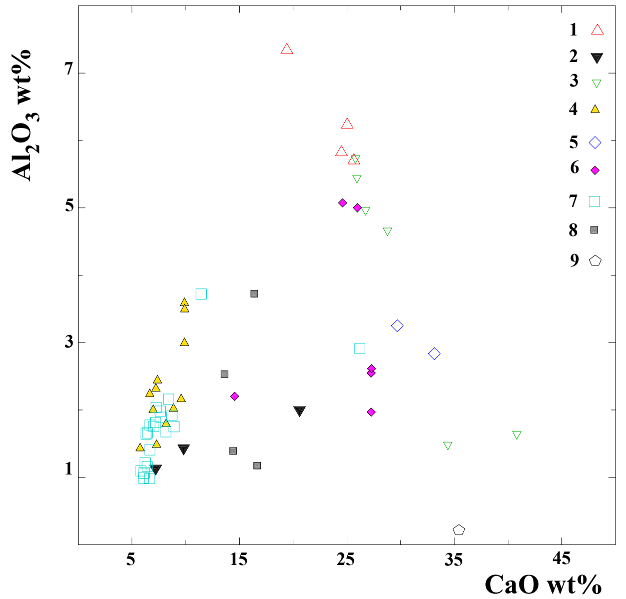

Figure 9. Variation of Al_2O_5 rate CaO wt% from the soil of Gafsa-Métlaoui Basin. 1: mud; 2: Selja; 3: Métlaoui; 4: M'Dhilla; 5: Sehib; 6: Tarfaoui; 7: Chott El Gharsa; 8: Soil control and 9: Phosphogypsum.

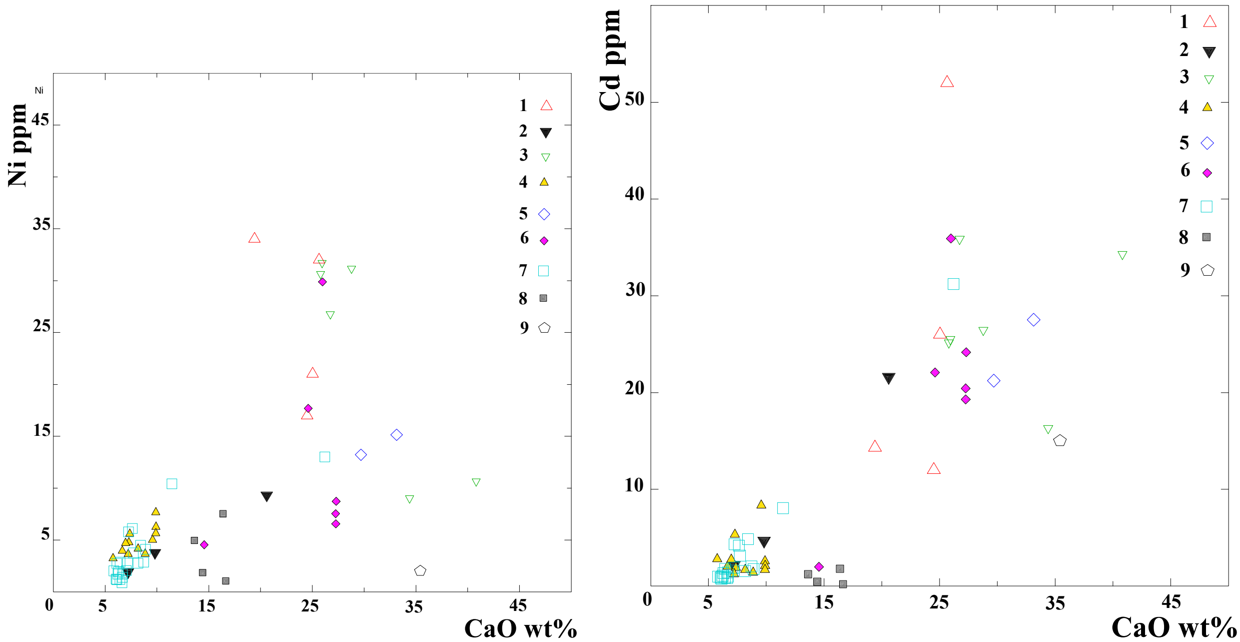

Figure10. Variation of Ni and Cd (ppm) versus CaO wt% from the soil of Gafsa Métlaoui Basin. 1: mud; 2: Selja; 3: Métlaoui; 4: M'Dhilla; 5: Sehib; 6: Tarfaoui; 7: Chott El Gharsa; 8: Soil control and 9: Phosphogypsum.

- The M'Dhilla soils present various P_2O_5 content's 1 up to 9% (MD6). The CaO shows levels ranging from 6 (MD5) and 10% (MD15). The highest value of MgO is recorded in the sample MD15 (1%). The phosphoric soils at M'Dhilla station were characterized by Cd values ranging between 1 and 8 ppm in MD6 and MD14 samples, respectively. Those of Cr ranged between 14.5 and 76 ppm. Zn varies between 2 and 260 ppm and Cu between 7 and 15 ppm. Ni shows low amounts with less than 8 ppm. Sr contents vary between 154 and 652 ppm in MD5 and MD6 samples, respectively.

- The Sehib soils show close values, with P_2O_5 above 14% and CaO of about 30%. The SiO_2 concentrations are ranging between 25 and 34%. The Al_2O_3, Fe_2O_3 and MgO contents are about 3, 1 and 2% respectively. The analyzed trace elements show high values with 21-27 ppm (Cd), 199-224 ppm (Zn), 207-242 ppm (Cr), 10 ppm (Cu) and 13-15 ppm (Ni).

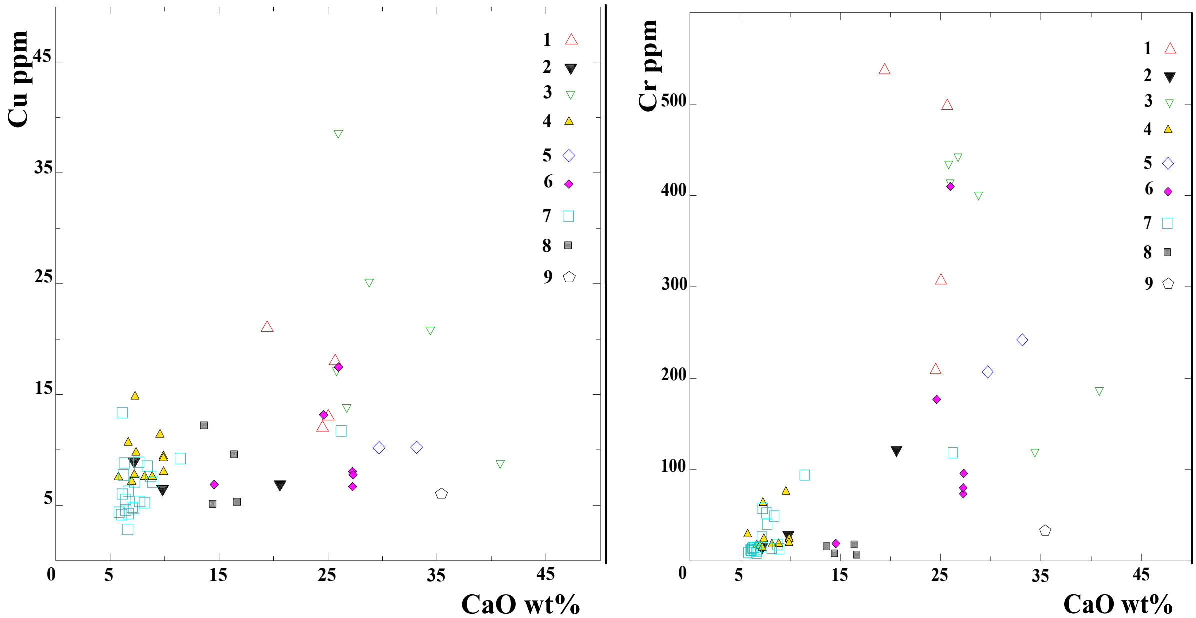

Figure11. Variation of Cu and Cr (ppm) VS CaO wt% from the soil of Gafsa-Métlaoui Basin. 1: mud; 2: Selja; 3: Métlaoui; 4: M'Dhilla; 5: Sehib; 6: Tarfaoui; 7: Chott El Gharsa; 8: Soil control and 9: Phosphogypsum.

- The Tarfaoui soils are mainly phosphoric, P_2O_5 ranging between 8 and 12% except sample T9 (0.78 wt%). CaO also shows values above 25 wt% except sample T9, which is about 14.5 wt%. SiO_2 concentrations range between 26 and 45% in samples TF7 and T2 respectively except T9 sample that shows silica enrichment (63%).

The Al_2O_3 results range from 2 % (T2) and 5% (TF7). The contents of Fe_2O_3 present values ranging from 1% (T2) and 2% (T6). MgO shows 1% contents. Trace elements at the Tarfaoui station are high except for the T9 sample, showing low values: 2 ppm (Cd), 74 ppm (Zn), 19 ppm (Cr), 7 ppm (Cu), 4.5 ppm (Ni) and 737 ppm (Sr). The maximum of Cd, Zn, Cr, Cu and Ni are recorded in the TF7 sample with 36, 276, 410, 17.5 and 30 ppm respectively. The highest value of Sr is about 898 ppm (T8).

- At Chott El Gharsa station, soils are depleted in phosphate with 1% approximately, except G2 sample taken from a reject-mound inside the wadi, which contains 10%. However, there is an enrichment of silica with amounts exceeding 70% except for G2 (37 wt% SiO_2 corresponding to the highest content of P_2O_5). CaO content varies from 6% (G4) to 26% (G2) and those of MgO are about 1 wt%. Al_2O_3 content ranges between 1 and 3.7 wt% (samples G6'). Fe_2O_3 shows low values; the maximum is recorded in the G1 sample (Fig. 1) with 1 wt%. The Cd ranges from 1 ppm (G15) to 31 ppm (G2). Zn content ranges from 3 ppm (G16) and 401 ppm (G2), with the exception of G1 and G0 two soil samples showing values above 1200 ppm. Cr shows varying levels with a maximum of 118 ppm (G2). The Cu and Ni values are low with a maximum of 14 ppm. Sr levels range from 157 ppm (G18) and 844 ppm in the G2 sample.

The samples, taken far from non polluted sites by the mud reflect the primary geochemical composition of the soil without phosphoric waste influence; the P_2O_5 maximum is about 0.3%. Thus, the mud provides a source of P_2O_5 in the soils sampled near the riversides. Moreover, trace elements show lower values than those found in soils collected near the riversides, except for copper and nickel. Ni and Cu reflect the natural geochemical background of the region; Sr contents remain high.

The comparison of trace elements analysis in soils sampled across the path of the discharge until Chott El Gharsa shows higher values than the normal values of heavy metals in soil reported by Cottenie (1982) and Henin (1983) such as for Cd and Cr, which are about 3 and 25 ppm respectively. The contamination seems to be related to the original releases washing industry of phosphate.

3.3. Heavy metal content and availability

Results (Table 2) show that metals (Cr, Ni, Cu and Cd) were virtually insoluble in the first extraction solution (in $CaCl_2$). In fact, the mobile fraction is almost zero (< 0.36%), indicating that the leaching under natural conditions is probably very low. The extraction with DTPA (2^{nd} extraction) does not allow the release of Cr and Ni. However, it generates an amount of metals (mainly Cd and Cu) suggesting that they are potentially available.

Zinc and strontium are more concentrated in the mobile phase, indicating that the solutions

containing these metals exist in natural conditions. These results reveal that the two fractions (mobile and mobilisable) containing acceptable trace elements can be released into the soil solutions.
In fact, the heavy metal potential availability can be expressed as follows: Sr > Zn > Cd > Cu > Ni > Cr.

Table 2. Heavy metal potential availability (expressed in percent of the total metal content) in the studied area. Each value represents the arithmetic mean of the 23 sampling points.

Metal	Mobile (%)	Mobilisable (%)
Cr	0.0023	0.0000
Ni	0.0000	0.1043
Cu	0.1509	1.5515
Cd	0.3502	4.3237
Zn	3.9046	0.9694
Sr	10.0091	3.9044

3.4. Metal concentrations in plants

Metal concentrations in plants vary with plant species (Alloway et al., 1990; Secu et al., 2008; Petrescu & Bilal 2007; Lăcătuşu et al., 2009). Plant uptake of heavy metals from soil occurs either passively with the mass flow of water into the roots, or through active transport, and crosses the plasma membrane of root epidermal cells. Under normal growing conditions, plants can potentially accumulate some metal ions in order of magnitude greater than the surrounding medium (Kim et al., 2003; Yoon et al., 2006).

In this study, a total of 30 species was collected from six localities from the site. Total Cd concentrations in plants range from 0.11 to 82 ppm, with the maximum in the leaves of *Anthemis stiparum* from Chott El Gharsa (Figs 12, 13).

The concentrations of Cd are high in different parts of the studied plants (Fig. 12), especially in the leaves. *Malva aegyptiaca* presents high values in the stems (maximum of 28.87 ppm). *Suaeda mollis* in different site shows low Cd concentration with maximum in leaves (2.83 ppm). *Atriplex inflata* in the Métlaoui, *Chenopodium chenopodioides*, *Malva aegyptiaca*, *Anthemis stiparum*, accumulate high levels of Cd in their parts. Cd concentractions in these plants reach phytotoxic levels (Kabata Pandias & Pandias, 1992). In fact, according to Solís-Domínguez et al. (2007) the normal concentration of Cd in leaf tissue ranges between 0.05–0.2 $mg.g^{-1}$, and the excessive or toxic values range from 5-10 up to 30 $mg.g^{-1}$.

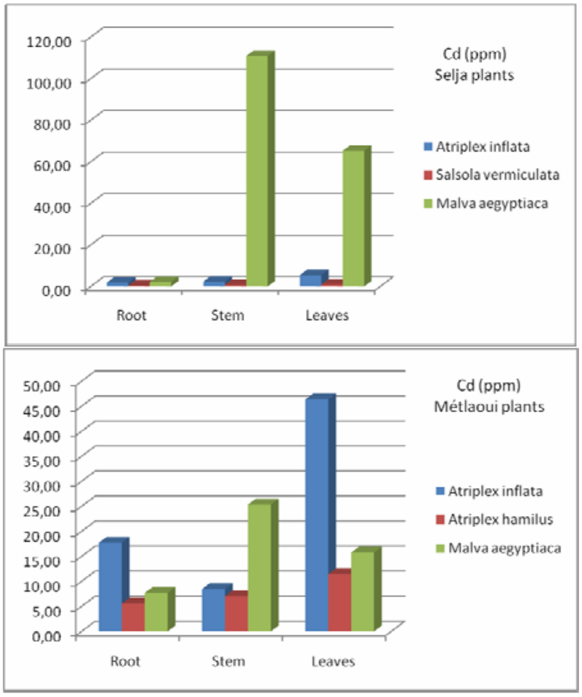

Figure 12. Variation of Cd in plant species from Selja and Métlaoui plants.

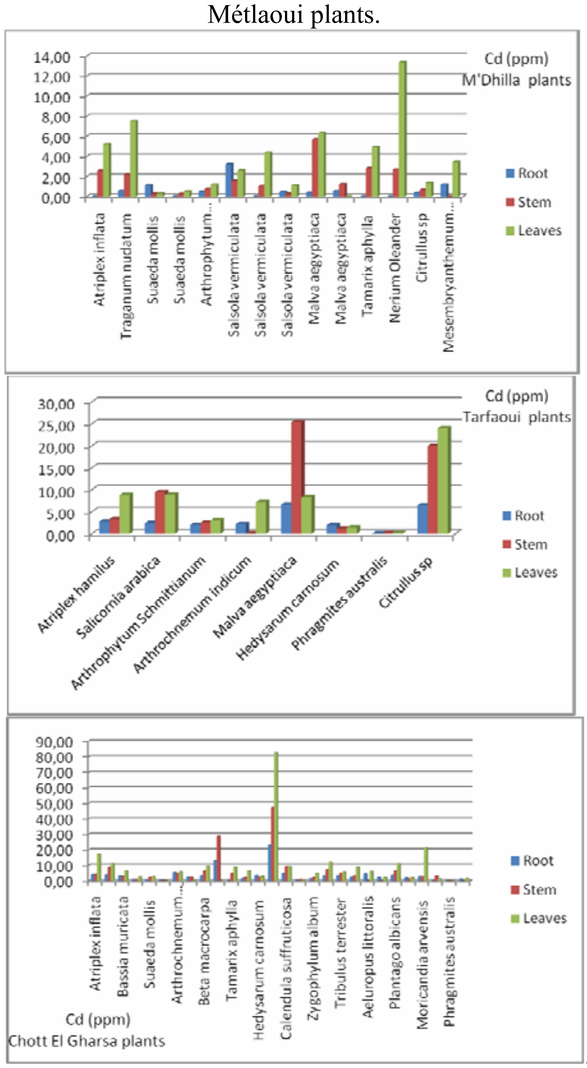

Figure 13. Variation of Cd in plant species from M'Dhilla, Tarfaoui and Chott El Gharsa plants.

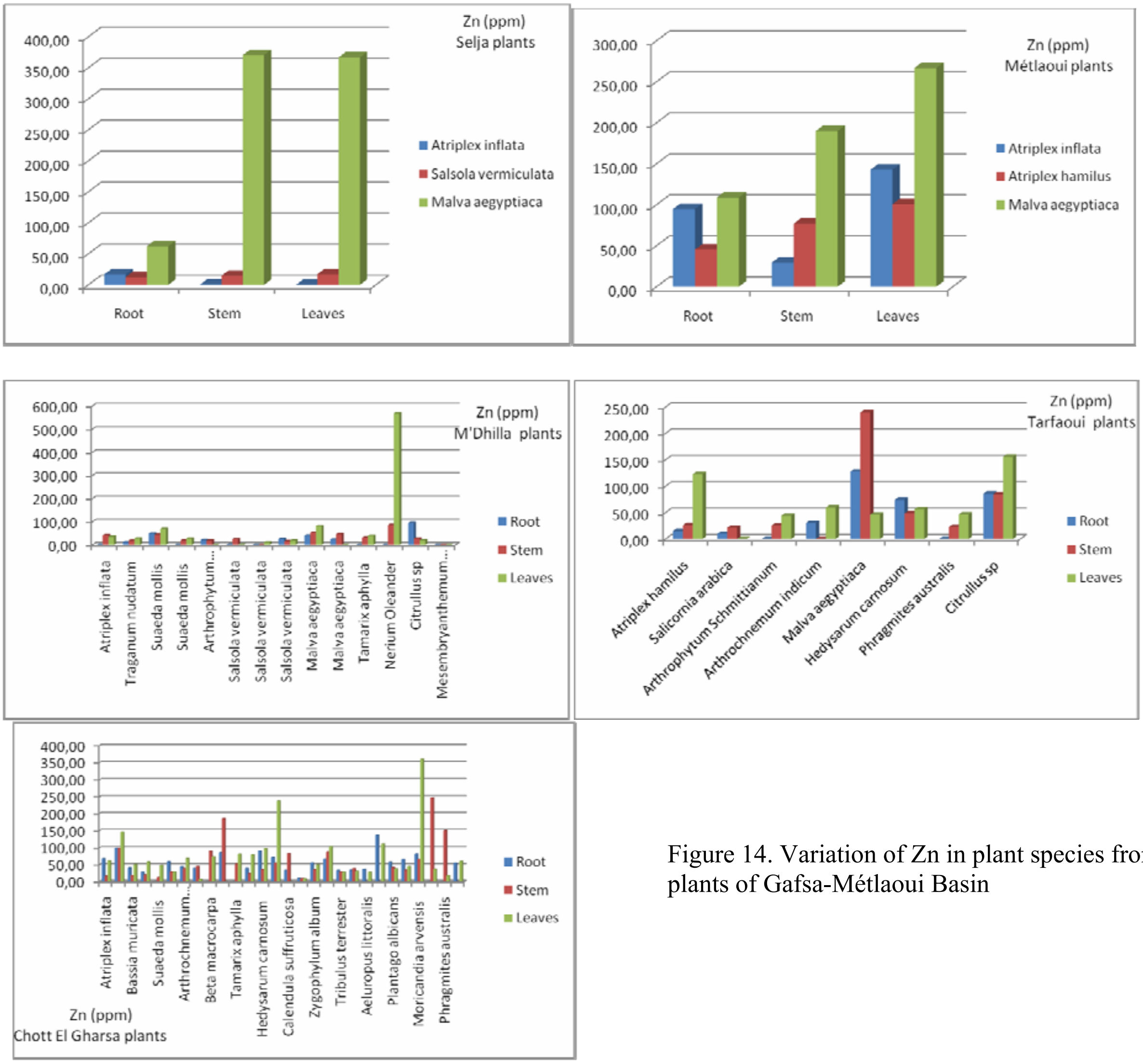

Figure 14. Variation of Zn in plant species from the plants of Gafsa-Métlaoui Basin

Table 3. Normal, deficiency, excessive and phytotoxic values (mg·kg–1) of heavy metals in vegetation (Kabata Pendias & Pendias, 1992)

Heavy metals	Normal values	Deficiency values	Excessive values	Phytotoxic level
Cd				5-30
Zn	27–150	10–20	100–400	70–400
Cr	0.1–0.5	-	5–30	75–100
Cu	5.1–30	2–5	20–100	60–125
Ni	0.1–5	-	10–100	100

Zinc concentrations in the plants vary from non-detectable to 567 ppm in leaves of *Nerium oleander* (Fig. 14). In addition, the leaves of *Moricandia arvensis, Malva aegyptiaca, Frankenia thymifolia, Anthemis stiparum* and, *Chenopodium chenopodioides* also enclode significant amounts of Zn (212-360 ppm).

According to Kabata Pendias and Pendias (1992), Zn in these plants is phytotoxic (Table 3).

Cr concentrations in different parts of the studied plants are low (Fig. 15). High amounts are recorded in the leaves of *Traganum nudatum* (15.86 ppm), roots of *Salsola vermiculata* in the M'Dhilla sector (MD2) with 10.15 ppm. Chromium in roots of *Aeluropus littoralis* is of 12.19 ppm. *Nerium oleander* shows the highest values of Cr in the roots (18.8 ppm) and leaves (174.7 ppm).

The Cu contents in the plants ranged from non-detectable to 51.73 ppm in leaves of *Nerium oleander* (Fig. 16).

Cu concentrations are within the standards except leaves of *Peganum harmala* (41.48 ppm) and *Nerium oleander* (51.73 ppm) with values in excess.

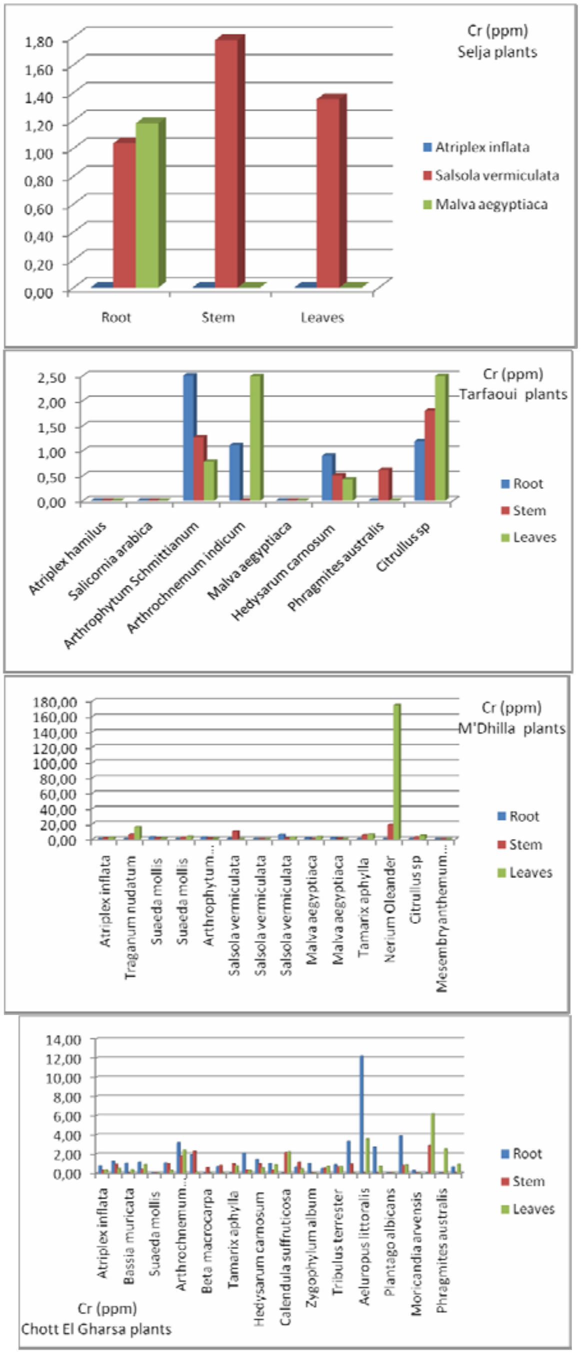

Figure 15. Variation of Cr in plant species from the plants of Gafsa-Métlaoui Basin.

Ni concentrations in the plants vary from non-detectable to 6.9 ppm (Fig. 17). Like Zn, Cr and Cu, the maximum values are found in the leaves of *Nerium oleander*. In all studied plants, the Ni concentrations are low. Sr shows high levels ranging from 6 ppm in leaves of *Suaeda mollis* to 2858 ppm in leaves of *Nerium oleander* (Fig. 18).

3.5. Accumulation and translocation of metals in plants

In this study, none of the plant species reveal metal concentrations higher than 100 ppm of Cd; or higher than 1000 ppm of Cu, Cr, or Ni, or 10000 ppm of Zn in the shoots. No one of them is hyperaccumulator (Baker & Brooks, 1989). However, the ability of these plants to tolerate and accumulate heavy metals may be useful for phytostabilization. Both bioconcentration factor (BCF) and translocation factor (TF) can be used to estimate a plant's potential for phytoremediation purpose after Yoon et al. (2006).

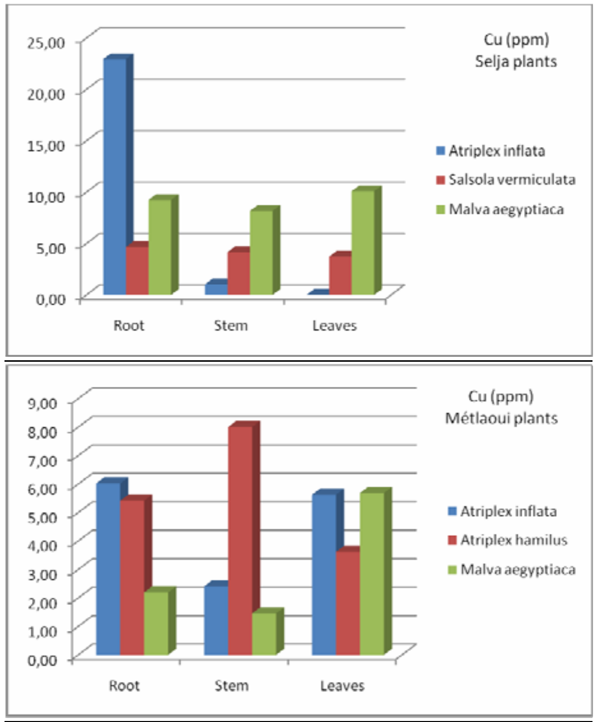

Figure 16. Variation of Cu in plant species from the Selja and Métlaoui plants.

A plant's ability to accumulate metals from soils can be estimated using the BCF, which is defined as the ratio of metal concentration in the roots to that in soil (Dowdy et al., 1997; Yoon et al., 2006; Gupta & Sinha, 2008). A plant's ability to translocate metals from the roots to the shoots is measured using the TF (Yoon et al., 2006; Gupta & Sinha 2007). According to MacFarlane et al. (2007), TF is defined as the ratio of concentration of metals in the leaves compared to those in the roots.
By comparing BCF and TF, we can compare the ability of different plants in taking up metals from soils and translocating them to the shoots. Plants exhibiting TF and particularly BCF values less than one are unsuitable for phytoextraction (Fitz & Wenzel, 2002).

Among the 30 species, *Anthemis stiparum,* had the highest BCF for Cd with 23.5 (Fig. 19) and a low TF (3.58). The translocation factor for Cd is greater than 1 in most studied plants; the highest value is about 30.7 in *Malva aegyptiaca* in Selja area. In Gharsa Chott: *Plantago albicans, Tribulus terrester, Peganum harmala, Arthrochnemum indicum* (in Gharsa and Tarfaoui), and *Bassia muricata* present BCFs and TFs greater than one.

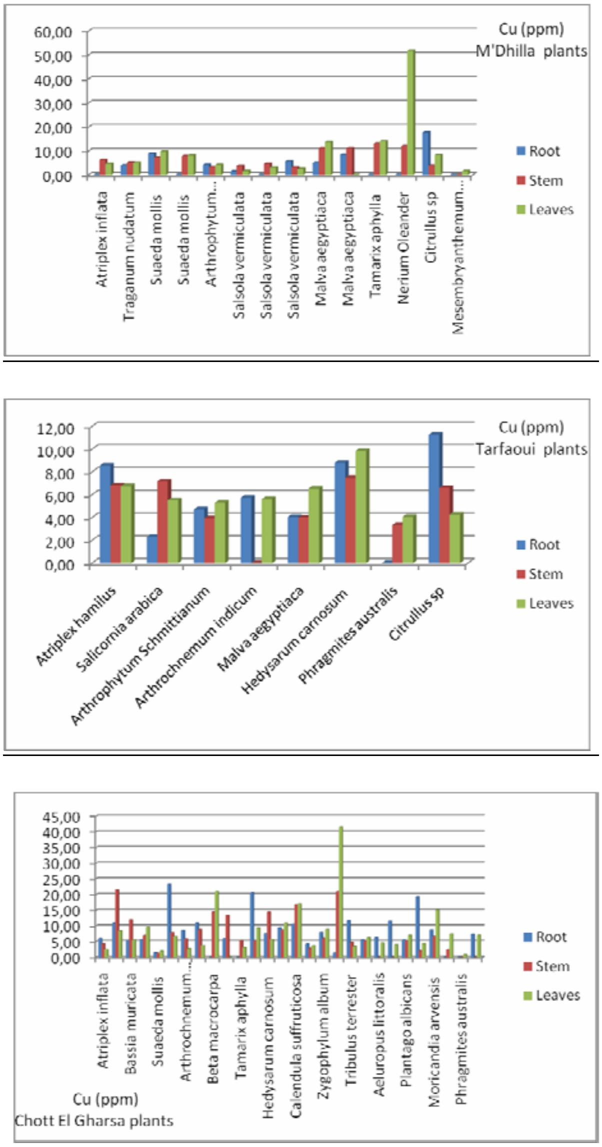

Figure 17. Variation of Cu in plant species from the M'Dhilla, Tarfaoui and Chott El Gharsa plants.

Chromium and nickel show low BCF values. Factor translocation is variable, the maximum is about 2.24 (Cr) in *Arthrochnemum indicum* (Tarfaoui site) and 5.58 (Ni) in *Malva aegyptiaca* (Selja site).

Anthemis stiparum, *Bassia muricata*, *Moricandia arvensis* and *Zygophylum album* in Gharsa site, and *Suaeda mollis* in M'Dhilla area, present BCF and TF > 1 for Cu; *Peganum harmala* reveals the highest value in TF for this element (TF=29.14).

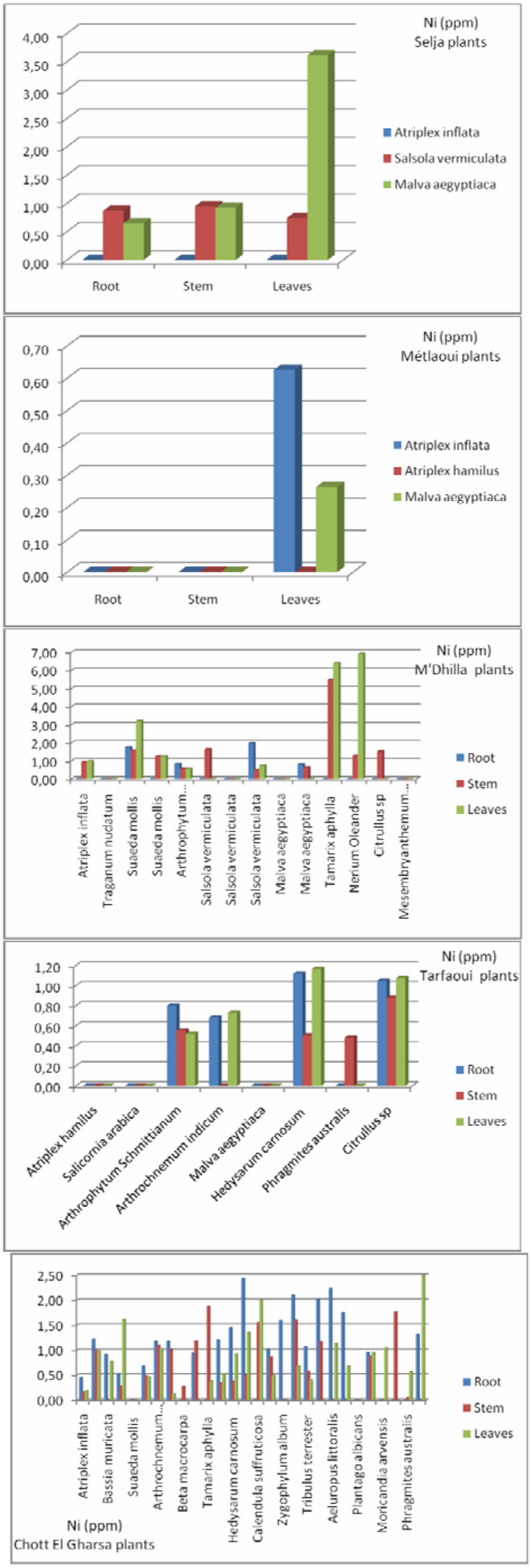

Figure 18. Variation of Ni in plant species from the plants of Gafsa-Métlaoui Basin.

Hedysarum carnosum, Calendula suffruticosa and *Tribulus terrester* (Chott El Gharsa site) and *Atriplex inflata* (Selja and Chott El Gharsa sites) and *Atriplex halimus* (Tarfaoui and Chott El Gharsa site) show high BCF and low TF.

Calendula suffruticosa, in Gharsa, has the highest BCF for Zn (9.83), *Frankenia thymifolia* reveals the highest value in TF (8.55) for Zn in Tafaoui area. Species that had high values in BCF and TF in this element are *Anthemis stiparum*, *Moricandia arvensis* and *Arthrochnemum indicum* in Chott El Gharsa and *Suaeda mollis* in M'Dhilla area. In Chott El Gharsa, *Calendula suffruticosa, Plantago albicans* and *Halocnemum strobilaceum* show high BCF and low TF.

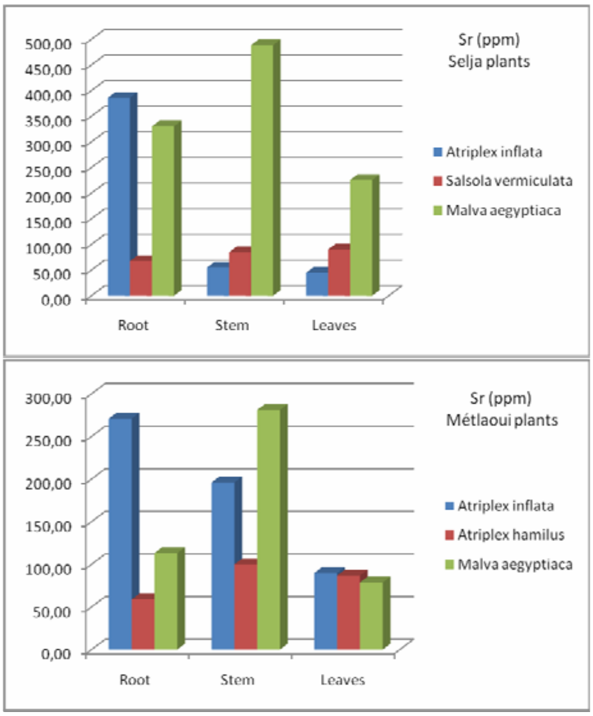

Figure 19. Variation of Sr in plant species from the Selja and Métlaoui plants.

4. DISCUSSION AND CONCLUSION

The majority of soils collected around the roots of plants at the Selja, Métlaoui, Sehib and Tarfaoui sites are enriched in phosphates from washing discharges. Samples soils in M'Dhilla and Chott El Gharsa are siliceous with very low levels of phosphate. Chemical analyses reveal that the collected soils at the riversides carrying the washing discharges include high metal concentrations. Comparison with maximum acceptable values (Cottenie, 1982 & Hennin, 1983) shows that these soils are contaminated mainly with Cd and Cr. M'Dhilla area is not polluted by mud but by the dust generated by the processing of phosphoric acid.

Atriplex inflata indicates that the bioconcentration factor is great for Sr (1.46), while *Citrullus* sp. reveals the highest TF (10.42) for this element.

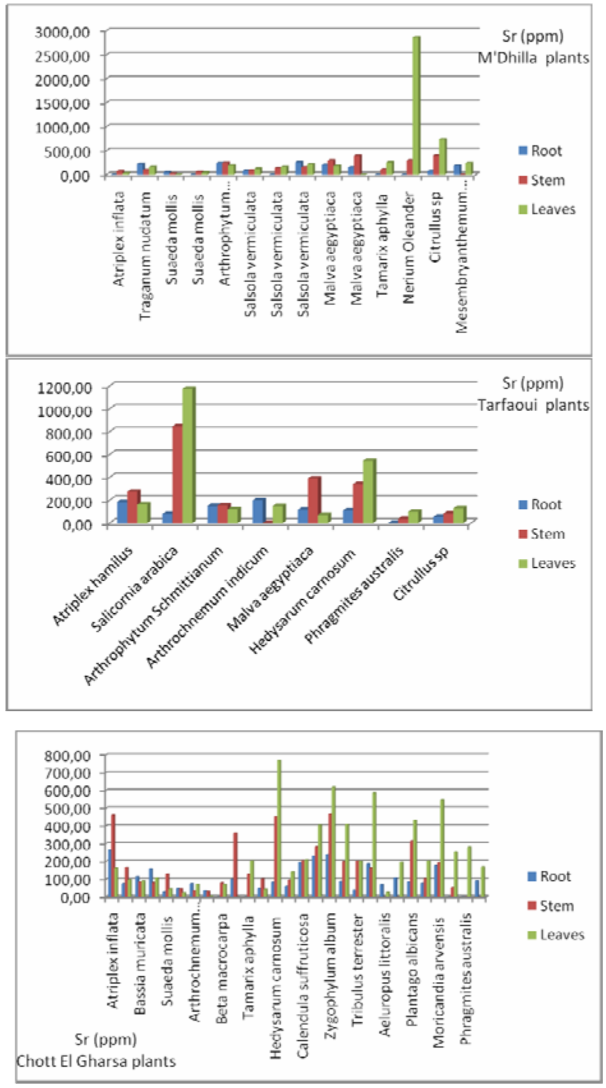

Figure 20. Variation of Sr in plant species from the plants of Gafsa-Métlaoui Basin.

Chott El Gharsa which receives all the releases providing from the laundries is located far away from these sources. Phosphate grains because of their high density are deposited along the hydrographic network. Clay minerals become dominant. Both stations show the lowest trace elements (metal) concentrations in the majority of soils but sometimes exceed the standards especially Cd and Cr in some samples.

The mobile fractions were insignificant while the mobilisable fractions, extracted with DTPA, have been a little more interesting (from about 4.3 % of total content for Cd to about 1.5% for Cu).

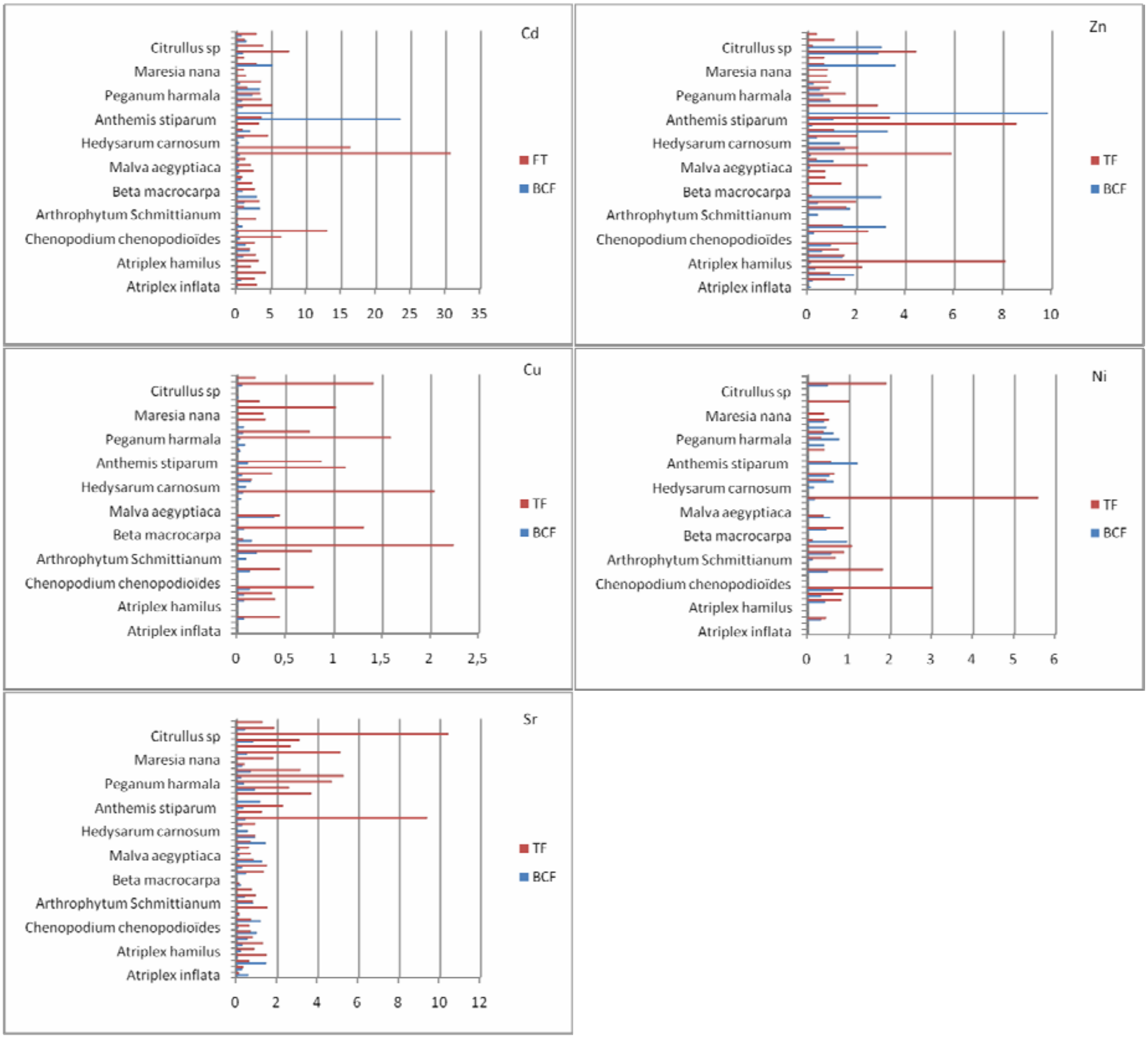

Figure 21. Variation of Bio-Concentration Factors (BCF) and Translocation Factors (TF) in plant species from the Gafsa-Métlaoui Basin

Cr and Ni are not extracted in both phases. Consequently, although these soils contain very high levels of potentially toxic heavy metals (mainly Cd and Cr); contaminants can be considered as quite insoluble and their leaching toward ground water due to rainfalls is probably very low. However, even though metals in soils are poorly leachable, their vertical transfer to above ground vegetation cannot be ruled out (Remon, 2006).

Indeed it is well known that plants can modify metal solubility (McLaughlin et al., 2000; Ge et al., 2000), notably through exudates release and/or modification of soil microbial activity. Consequently, results of sequential extraction procedures are not inevitably correlated with the levels of heavy metals actually accumulated in plants (Remon, 2006).

In this study, the potential mobilization of trace elements seems to decrease as follows: Sr > Zn > Cd > Cu > Ni > Cr. The absorption of these elements in plants is variable from one species to another, but the majority of plants shows that the accumulation of metals followed this order: Sr > Zn > Cd > Cu > Cr > Ni, indicating that the metal release in the soils correlates with their absorption by the plants.

The main of studied plants show excess values in trace elements and sometimes in the range of phytotoxic levels; this result reveals that the studied plants are tolerant to these elements.

Cadmium is a toxic element for plants (Das et al., 1997; Sanita di Toppi & Gabrielli, 1999) and few species can tolerate their high concentrations in the soil. The contents of this element in the studied plants vary between species, but the values are high. *Anthemis stiparum* and *Chenopodium chenopodioides* are the two species with the most cadmium accumulation. The main species concentrate cadmium in their leaves but, *Malva aegyptiaca* accumulates high concentration of this element in the stems.

Zinc, copper and nickel are essential elements for plants (Welch, 1995; Reid, 2001; Rengel, 2004; Marcic, 2005), but they may be toxic in high dose; some plants can tolerate high levels. Zinc, in this work shows normal values with the exception of some species that tolerate high rates. *Nerium Oleander*, *Moricandia arvensis*, *Malva aegyptiaca, Frankenia thymifolia*, *Anthemis stiparum* and *Chenopodium chenopodioides* accumulate high concentrations in their leaves.

Chromium is a toxic metal for plants; *Nerium oleander* accumulates high amounts of this element. Copper is different of chromium by the fact that it is an essential element of the mineral nutrition of plants (Punz & Sieghard 1993; Raskin & et al., 1994). It is essential for their growth and metabolism (Loué, 1993; Marschner, 1995; Clemens, 2001) and in case of failure can cause problems for their growing. *Nerium oleander* accumulates the maximum value of Cu. The levels of Ni are in the standards. Strontium has the highest levels of analyzed trace elements; *Nerium oleander*, *Salicornia arabica* and *Zygophylum album* contain the most Sr accumulations.

It is noted that *Nerium oleander* absorbs high levels of Cd, Zn, Cr, Cu and Sr in their leaves.

The process of phytoextraction generally requires the translocation of heavy metals to the easily exploitable, such as leaves. By comparing BCF and TF, we can estimate the ability of different species for the metals, from soil and their translocation to the aerial parts. The species that show values of TF and especially BCF < 1 are inadequate to the phytoextraction (Fitz & Wenzel, 2002). Only those species that show values of BCFs and TFs greater than one, have the potential to be used for the phytoextraction (Yoon et al., 2006). In this present work, many species have BCF and TF greater than one. None of the plants were suitable for the phytoextraction because no hyperaccumulator was identified.

Heavy metal-tolerent species with high BCF and low TF can be used for phytostabilisation of contaminated sites, together with a vegetative cover (Yoon et al., 2006). Examples of such plants in our study included *Anthemis stiparum* for Cd; *Calendula suffruticosa, Plantago albicans*, and *Halocnemum strobilaceum* for Zn and, *Hedysarum carnosum, Calendula suffruticosa, Atriplex inflata, Atriplex halimus* and *Tribulus terrester* for Cu. Phytostabilisation can be used to reduce the mobility of metals in contaminated soils (Susarla et al., 2002). This process uses the ability of plant roots to change environmental conditions via root exudates. Plants can immobilize heavy metals through absorption and accumulation by roots, adsorption onto roots, or precipitation within rhizosphere. This process reduces the metal mobility and leaching into ground water, and also reduces the metal bioavailability for entry into the food chain.

Among those species collected from the contaminated site, the plants most effective in the translocation of metals are *Malva aegyptiaca* (TF=30.7) for Cd, *Frankenia thymifolia* (TF=8.55) for Zn, *Peganum harmala* (TF=29.14) for Cu and *Cittrulus* sp. (TF=10.42) for Sr.

The absorption of Cr and Ni by roots and their transfer to the stems and leaves is very low in most plants analyzed.

These species tolerate high levels of trace elements, play an important role for soil remediation at the same time they are toxic to the food chain when consumed as forage.

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